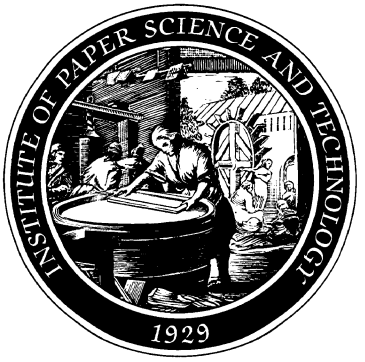

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HAPs Release from Wood Drying

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HAPs Release From Wood Drying

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Abstract

Hazardous Air Pollutant (HAP) profiles from drying softwood and hardwood flakes (for the manufacture of oriented strand board) are very similar, indicating that they originate through a common mechanism, the breakdown of wood tissue. Hence, the strategies employed to reduce VOC (volatile organic compound) emissions from hardwood can also be extended to decreasing HAPs from softwood. Drying aspen flakes in the field and in the laboratory gives rise to different VOC species, and direct extension of laboratory data to the field may prove difficult. Formaldehyde emissions from drying fresh aspen flakes are lower than those from stored material; the opposite effect occurs for methanol and the other aldehydes. HAPs evolved from drying pine flakes surge sharply at 5-10% moisture content during drying at 130-160°C. Emissions of methanol, formaldehyde, pentanal, and hexanal all begin simultaneously, with the release of methanol and formaldehyde being the most sensitive to dryer temperature. Hence, the nature of the VOC mix will be at least partly governed by the dryer temperature. Pine and aspen give rise to similar HAPs profiles during either drying or pressing flakes that are already dried.

Introduction

VOCs released from hardwood and softwood differ both in the nature and in the quantities of material evolved. Hardwood VOCs are principally degradation products that arise from the thermal breakdown of wood. They include methanol, formaldehyde, and other compounds designated by the U.S. EPA as Hazardous Air Pollutants, or HAPs (1). Softwood releases a much larger quantity of VOCs, most of which are terpenes (2). However, since wood tissue may also be subject to thermal breakdown during softwood drying, the same suite of VOCs evolved from hardwood may also be evolved from softwood. In other words, in addition to its predominantly terpene load, softwood VOCs may also include HAPs.

We have shown that drying hardwood to final moistures of 5% or more (as opposed to the much lower values that is common industry practice) can lead to a dramatic decrease in VOCs (3). Wood is evaporatively cooled by the departing moisture as it dries. The cooling effect is lost late in the process when the water is mostly gone, the wood tissue temperature rises, wood decomposition begins, and VOCs are evolved. The VOCs rise very sharply indicating that the decomposition is associated with a high activation energy (3); increasing the final moisture content (MC) from 2% to 5% can reduce VOCs by over 60%. These findings have been inde-

pendently confirmed for formaldehyde, whose evolution increases rapidly with drying temperature (4).

The VOC-dryer temperature curve is more gradual for softwood since pinene, the principal VOC constituent, is released more through vapor pressure and Henry's Law considerations, and not from wood breakdown (2). Hence, while the dependence of the *total* VOCs from softwood on dryer temperature may be quite moderate, that of the smaller HAP subgroup should be just as sensitive as that from hardwood. Given that HAPs are under regulation (5), it is important to understand the factors that govern the release of these compounds.

Experimental

Pine flakes for the production of oriented strand board were obtained from the Georgia-Pacific Dudley, NC, mill; aspen flakes were provided by the Potlatch Grand Rapids, MN, facility and the Georgia-Pacific, Woodland, ME, mill. The flakes were dried at 105°C for work that required dry furnish. The tube furnace used for drying flakes in the laboratory has been described earlier (2, 3). Briefly, air (0.25 L/min) is directed over 4-7 g. of furnish placed in an aluminum foil boat in a heated ceramic tube, and the VOCs are stripped from the air stream in either chilled water (for the determination of methanol and formaldehyde) or in a methanol trap (for collecting the other organics).

Formaldehyde recoveries were first established by heating a known amount of formaldehyde (12.5 μg/mL) in the tube furnace at 160°C for 0.5 hr, collecting the emissions in 20 mL of either chilled water or 1% sodium bisulfite solution, and analyzing the trapped material by the chromotropic acid method (6). Water was used in situations where the trapped material was also analyzed by gc for other components; an interference was observed in the presence of bisulfite. Formaldehyde recoveries were 95% in water and 103% in bisulfite. Methanol was determined by gc, and its recovery through the oven/trap assembly was 95%. Since formaldehyde was inseparable from methanol under our gc conditions, the two were quantified together and the methanol determined by subtracting out the independently-measured formaldehyde, after normalizing for differences in gc response factors. Pentanal and hexanal were collected in chilled methanol; their recoveries were 90-94%. All emissions data are reported on a dry basis.

Flake temperature was measured during drying in a 160°C oven by attaching a thermocouple to the surface and measuring the time-temperature curve. The section of the thermocouple not in contact with the wood was insulated. Since flake weight loss and temperature could not be simultaneously measured, equivalent batches of flakes were dried under similar conditions for varying periods and a time-MC curve was determined. The temperature-MC curve was then obtained by combining the two sets of data.

VOCs were collected in the field (Woodland, ME, during August 26-28, 1998), by inserting a heated sample probe into the center of the dryer stack. A heated sample pump and line was used to convey the gases to chilled impingers, each containing 20 mL of water. Two impingers connected in parallel were used; one contained organics-free water for methanol collection, while 1% sodium bisulfite was used in the other for trapping formaldehyde. Each collection was run in duplicate for 30 minutes. A second sampling assembly was used to simultaneously record total hydrocarbon emissions through a Method 25A determination (7). The flow through each

impinger was controlled at 0.4 L/min, with the flow meters connected after the impingers to prevent deposition in the flow meter.

VOCs released during pressing operations originate from both the wood and the applied resin. In order to determine volatiles released from wood alone, resin was not added, and flakes were placed in a steel foil bag (0.002 in. thick 309 high-chromium stainless steel) with inlet and outlet tube connections. The bag was then placed between the top (200°C) and lower platens (90°C) of an electrohydraulic press (8) and pressed at 1,000 psi for 3 minutes to a thickness of 1/8-inch, which corresponds to approximately 48 lb/ft^3. Air passed through the bag at 0.5 L/min was bubbled into a trap containing either chilled water or methanol. Airflow was continued for an additional 5 minutes after pressing to purge any residual VOC from the bag. The trapped samples were analyzed as described above.

Results and Discussion

Laboratory and field emissions from green aspen

Some of the compounds released from aspen flakes during drying at 160°C for 2 hours are listed in Table 1. Since the wood dries in about 20 minutes under these conditions, these values include emissions from both green and dry wood. This was done to ensure capture of compounds released from both early and late drying. Field VOC data collected at four 30-minute intervals from the core dryer at the Georgia-Pacific mill in Woodland, ME, are reported in Table 2. Comparison of the Method 25A and compound-specific results is qualitative, at best, for two reasons. First, the Method 25A response for methanol and formaldehyde is quite low. Second, the mill includes about 15% pine in its furnish (3) which would approximately double the Method 25A values on account of the terpenes present. If the Method 25A values are halved on this account (3), then the correspondence between the Method 25A and the speciated VOC values is quite good.

There were surprisingly large differences in the nature of the VOCs from laboratory and field-derived VOCs. Pentanal and hexanal, which constitute half of the total emissions in laboratory work (Table 1), were not found in the field (mdl=4 ppm). Aldehydes have frequently been measured in previous laboratory drying or pressing work. For example, Carlson et al. found hexanal to be the major VOC constituent during pressing of aspen strand (9), and Wang and Gardner (10) obtained similar results from pressing Southern pine. Conversely, ethanol, a major component of the field VOCs, was absent in the laboratory sample. Ethanol has frequently been found in unpublished fieldwork (11).

Table 1: VOC emissions from aspen

	avg. (μg/g)[1]	std dev (μg/g)
methanol	100	9
pentanal	70	20
hexanal	30	3
formaldehyde	11.3	
unknowns[2]	53	5

[1]n=5; [2]determined assuming a gc response factor of pentanal

Table 2: VOC concentration (ppm) in the stack gases of the core dryer at Woodland					
run	**formal-dehyde**	**metha-nol**	**ethanol**	**total trapped VOCs**	**method 25A VOC**
1	2.93	4.12	5.49	12.5	29.2
2	4.62	5.53	6.41	16.6	23.9
3	2.89	8.61	5.90	17.4	37.3
4	4.20	12.1	9.22	25.5	50.8
avg (avg. dev.)	3.7 (0.8)	8 (3)	7 (2)	18 (5)	35 (6)

Table 3: Emissions from aspen (μg/g, dry basis) after storage[1]						
days of storage	**methanol**	**acetone**	**pentanal**	**hexanal**	**formalde-hyde**	**n**
160°C						
10	126 (7)	25 (5)	42 (9)	120 (10)	11 (2)	4
30	100 (10)	20 (3)	19 (2)	40 (10)	43 (2)	2
55	100 (20)	15 (2)	11 (2)	26 (7)	35 (1)	2
130°C						
10	59 (3)	19 (3)	2 (0)	27 (4)	1.0 (0.3)	2
30	10 (3)	4 (0)	5 (1)	15 (2)	3.3 (0.2)	2
[1]collected in water; the values in brackets are average deviations						

The laboratory results are consistent, at least to the extent that similar compounds have consistently been found across different furnishes and processes, and it is likely that differences between laboratory and field measurements originate from differences in drying conditions. Large temperature and humidity gradients exist in the field, and it is very difficult to reproduce these in the laboratory. For example, aldehydes are relatively unstable, and it is possible that they could have degraded in the air stream. Differences may also be anticipated across samples taken from various commercial facilities, where dryer temperatures and profiles can vary appreciably.

In order to determine the effect of furnish storage time on emissions from aspen, flakes were stored cold, and VOCs periodically measured from drying over 1 hr. at 160°C. The results, listed in Table 3, show that drying stored flakes leads to more formaldehyde, suggesting that formaldehyde is biologically or chemically generated during storage. The generation of formaldehyde during lignin biodegradation is well known (12). In contrast, emissions of the other VOCs decrease upon storage, with the decrease being most pronounced for pentanal and hexanal. Corresponding Method 25A emissions also show a decrease in VOCs upon storage.

Emissions from green pine

The surface temperature of pine flakes during 160°C drying is provided as a function of MC in Figure 1. As discussed above, the temperature levels off at about 90°C during the evaporative cooling period and then rises during the later falling rate period. Although terpenes are the

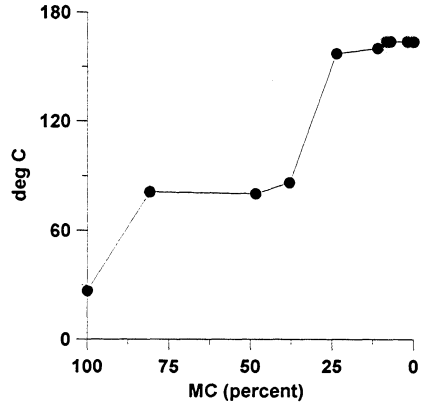

Figure 1: Surface temperature profile of pine flakes during drying at 160°C.

principal constituents of emissions from pine, the compounds released from aspen should also be found in pine VOCs, if indeed they also derive from the breakdown of wood tissue.

While the rise in VOCs observed from drying aspen is sharp, that from pine is much more gradual (2), since the terpenes, the major component of pine VOCs, are not degradation products. However, the suite of compounds that arise from the breakdown of pine tissue should be strongly temperature-dependent, just as in the case of aspen. If so, then drying softwood to lower wood tissue temperatures would substantially reduce the amount of methanol and aldehydes released, although the decrease in *total* VOC emissions would be much more modest.

In order to establish that methanol and aldehydes emerge principally during late drying, pine flakes of varying final moisture were dried at different temperatures. The results shown in Figure 2 confirm that the bulk of the release occurs when the wood is almost dry and that overdrying should substantially increase these emissions. The clear link between formaldehyde and the other traces in Figure 2 suggest that they arise from the same process. However, since formaldehyde increases upon storage, there are probably two sources of formaldehyde: biological and thermal.

The VOC surge occurs slightly earlier (10% MC) at 160°C as compared to about 5% at 130°C, since the VOCs start being released at about 130°C as the flake warms to the oven set temperature of 160°C. The effect is exaggerated at 200°C, where the VOC rise starts even earlier, since the flakes start decomposing at temperatures well below 200°C; i.e. the higher dryer temperature puts the surface tissue into the falling rate zone, although appreciable moisture still remains in the flakes. The position of the surge for methanol and formaldehyde tracks those for the higher aldehydes, but much more methanol and formaldehyde are evolved at the higher temperature. Clearly, the VOC species produced will depend upon the drying conditions, with higher temperatures favoring methanol/formaldehyde emissions. That all of the VOCs surge from the same MC value suggests a common source, almost certainly the thermal breakdown of wood tissue. The finding that the VOC mix changes with temperature indicates that the smaller compounds on the one hand, and the larger aldehydes on the other, arise from different pathways along the degradation of wood tissue.

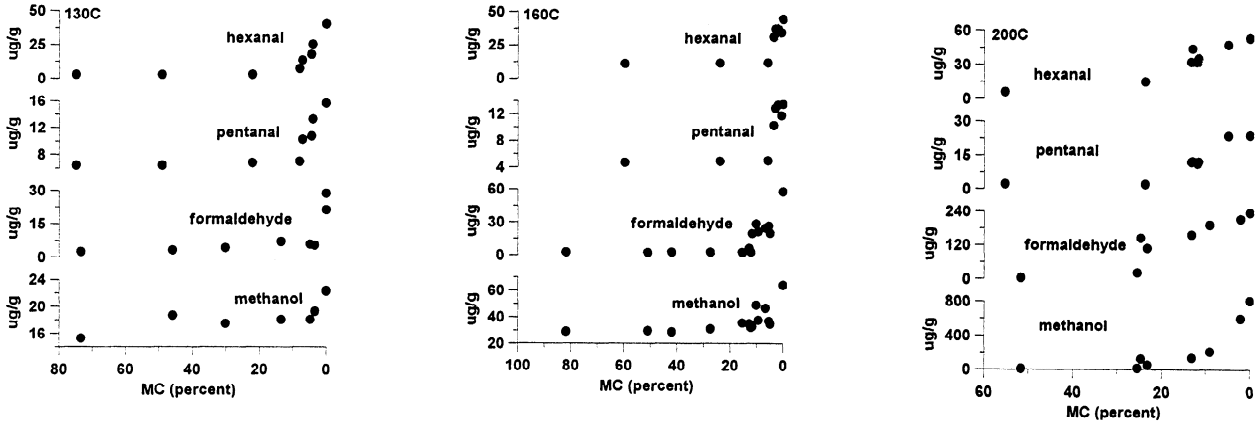

Figure 2: Profiles of selected constituents released from drying pine flakes at 130, 160, and 200°C.

The Figure 2 result that methanol and the aldehydes are released late suggests that they could be drastically reduced if the temperature was reduced, and if drying was terminated just before the surge, i.e., a slightly wetter furnish was accepted. This practice would require a resin capable of handling the higher moisture, but this is already being done at the Georgia-Pacific Woodland facility (3) and it should be easily extended to softwood. The release of terpenes, the major constituent of softwood will be reduced minimally, but large reductions in HAPs could be taken at relatively low cost. However, HAPs reduction will be difficult at temperatures exceeding 160°C, since the wood would still be appreciably wet when HAPs evolution begins, i.e. the surface will dry too rapidly.

The Figure 2 profiles differ sharply from those of the terpenes, where two signals are observed (13). The first is sharp and arises early and reflects material on the surface of the wood. The second is broader and starts when evaporative cooling tails off. Wood breakdown is not involved for terpene release, which is akin to a distillation process, in contrast to the Figure 2 components, which arise from tissue degradation.

Emissions from dry pine and aspen

Emissions collected from dry pine and aspen flakes heated at 130, 160, and 190°C, respectively, for 30 minutes are illustrated in Figure 3 and demonstrate that the total water-soluble VOCs increase with increasing dryer temperature. The VOC profiles between the two species are remarkably similar, confirming that they arise from the thermal degradation of wood tissue. A similar correspondence between softwood and hardwood has been observed in the field in an extensive multi-facility study (14). Since the furnish dries in about 20 minutes at 160°C, it is clear that overdrying will enhance methanol release. Means to minimize this, e.g., through green-screening (to remove the faster-drying fines), or drying to slightly higher moisture, should reduce methanol emissions.

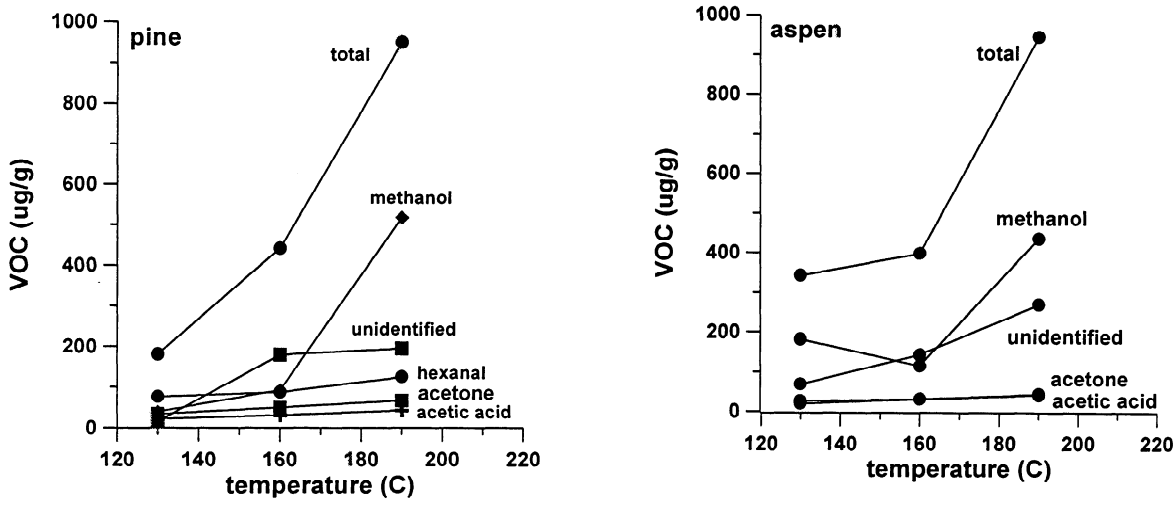

Figure 3: Water-soluble VOCs from dry pine and aspen.

Table 4: VOCs (μg/g) collected in water during 3 minutes of pressing[1]							
	acetone	**meth-anol**	**formal-dehyde**	**pentanal**	**hexanal**	**pinene**	**total**
water trap[2]							
pine	3±1 (5)	7±6 (4)	1.1±0.5 (4)	1.0±0.3 (3)	4±2 (3)		13±3 (5)
aspen	1.2±0.7 (8)	4±2 (8)	0.5±0.4 (7)	1.1±0.8 (8)	6±5 (7)		15±8 (8)
methanol trap[3]							
pine	3.0			3.0	14	35	55
aspen	15.1			4.3	24		34
[1]increasing press time to 5 minutes gave similar results; [2]the bracketed values are average deviations; [3]the bracketed values are standard deviations.							

Emissions from pressing pine and aspen

With the exception of pinene, the similarity in dryer emissions between softwood and hardwood extends to releases from pressing as shown in Table 4, indicating that they too arise from the thermal degradation of wood. Formaldehyde emissions from pressing either hardwood (9) or softwood (10) increase linearly with press time and exponentially with temperature, indicating that they arise from thermal degradation. Modifying pressing conditions to minimize the temperature rise or using higher MC furnish should lead to reduced emissions from the wood furnish.

Control implications

Although the VOC composition changes with both species and drying conditions, methanol and formaldehyde, the two major HAPs emitted from both hardwood and softwood, are always released in both laboratory and fieldwork under conditions where wood tissue thermally

degrades. Since these HAPs constitute much of the total VOC package from hardwood, drying to higher MC and pressing higher-moisture flakes should reduce the quantity of HAPs emitted. The Georgia-Pacific Woodland, ME, mill has won regulatory approval to adopt this practice in lieu of end-of-pipe control devices. We have now shown that a similar strategy can also reduce HAPs from softwood, although the total VOC load (mainly terpenes) will remain relatively unaffected. The economic, energy, and environmental trade-off is under study.

Acknowledgment

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